Calculation of Thermodynamic Properties of Fluid Mixtures through a Generalised Helmholtz Equation

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Helmholtz equations of state have become the preferred approach for the development of accurate equations of state for pure substances. In this scheme, the reduced Helmholtz energy A/RT is expressed as:

$$\alpha(\omega,\tau) = A/RT = \alpha^{\mathrm{r}}(\omega,\tau) + \alpha^{\mathrm{id}}(\omega,\tau), \tag{1}$$

where R is the gas constant, T is the temperature, ω and τ are the dimensionless reduced density and the inverse reduced temperature, respectively, and $\alpha^{\mathrm{r}}(\omega,\tau)$ represents the difference between the reduced Helmholtz energy of the real fluid and that of the ideal gas $\alpha^{\mathrm{id}}(\omega,\tau)$, or the residual part.

Such highly successful Helmholtz formulations for the representation of the thermodynamic properties of pure components can be easily extended to multicomponent systems through the rigorous thermodynamic relation:

$$\alpha(\omega,\tau,\mathbf{x}) = \sum_{i=1}^{N} x_i \alpha_i(\omega,\tau) + \alpha^{\mathrm{E}}(\omega,\tau,\mathbf{x}), \tag{2}$$

where $\alpha_i(\omega,\tau)$ is the Helmholtz energy of component i, x_i is the mole fraction of component i, $\mathbf{x}$ is the composition vector for the whole system, N is the number of components in the mixture of interest and $\alpha^{\mathrm{E}}(\omega,\tau,\mathbf{x})$ is the excess Helmholtz energy.

There are however two important questions to be resolved before implementing this approach. The first one relates to the reducing parameters of the density and the temperature and the second is the excess Helmholtz energy contribution for which no theoretical model is available for its determination.

In this paper we report on how these questions have been addressed and how the model represented by equation (2) was implemented. The performance of the model is assessed by comparison of its representation of the thermodynamic properties of (methane + ethane) for which accurate experimental data in both the single and two-phase regions are available.